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Mathematical solutions and numerical models employed for the investigations of PCMs' phase transformations

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ABSTRACT

Latent heat thermal energy storage (LHTES) has recently attracted increasing interest related to the thermal applications, and has been studied by researchers using theoretical and numerical approaches. The heat transfer mechanisms during the charging and discharging periods of the phase change materials (PCMs) and two basic problems for phase transformations have been discussed in this paper. 1D, 2D and 3D popular mathematical solutions based on the heat transfer mechanisms of conduction and/or convection have been analyzed. Then, various numerical models for encapsulated PCMs in terms of macro-encapsulated PCM and micro-encapsulated PCM were investigated. The numerical simulation of heat transfer problems in phase change processes is complicated and the achieved results are approximate according to a number of conditions. The accuracy of numerical solution depends on the assumptions that are made by the authors. Therefore this review will enable the researchers to have an overall view of the mathematical and numerical methods used for PCM's phase transformations. It offers the researcher a guideline of selecting the appropriate theoretical solutions according to their researches' purposes.

Contents

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Nomenclature

f	melt fraction
c	specific heat at constant pressure
H	total volumetric enthalpy (J/m^3)
h	average heat transfer coefficient (J/kg)
k	thermal conductivity (W/mK)
L	latent heat (J/kg)
St	Stefan number
t	time (s)
T	temperature (K)
T_m	melting temperature (K)
T_s	initial temperature of solid PCM (K)
T_0	constant temperature imposed on $x=0$ (K)
P	present nodal point
$\delta(t)$	position of liquid–solid interface
x, y	Cartesian coordinates

Greek symbols

Δ	difference
$\propto$	thermal diffusivity of PCM (m^2/s)
η	dimensionless number used in derivations as a temporary substitution
λ	dimensionless number in solution to Neumann problem, liquid fraction
ρ	density (kg/m^3)

Subscripts

l	liquid
s	solid
i	ith spatial step
j	jth time step
eff	effective

1. Introduction

Due to the attractive features of latent heat storage, phase change materials (PCMs) are mainly used to store energy at a fixed temperature (melting/solidification temperature) with high energy density [1]. PCMs have been applied in various systems and aspects such as energy storage systems, free ventilation, free heating and cooling for buildings, spacecraft, food, medicine conservation, smoothing the peaks of exothermic temperature in chemical reactions etc. PCMs are a better choice comparing to the sensible heat storage in applications, because of its nearly isothermal storing mechanism and high storage density. PCMs absorb abundant energy through the phase transition and release the stored energy. Table 1 compares the typical properties of different thermal storage materials tested at the room temperature. It indicates that PCMs can save 92.8% of mass and up to 90% space to store the same amount of thermal energy comparing to the sensible thermal materials such like concrete and water.

Therefore, PCMs attract the researchers' interesting in practically individual and incorporation applications in different engineering fields. The possibility, feasibility, thermal performance and economic analysis of using PCMs call a series of theoretical and experiential investigations, the mainly two methods used to research the thermo-physical parameters of PCMs and interrelated systems.

Table 1
Properties comparison of different thermal storage materials.

Property	Unit	Materials			
		Concrete (sand and gravel)	Water	Organic PCM	Inorganic PCM
Density	[kg/m^3]	2240	1000	800	1600
Specific heat capacity	[kJ/kg K]	1.1	4.2	2.0	2.0
Latent heat	[kJ/kg K]	–	–	190	230
Storage mass for 10^6 kJ, avg	[kg]	60,000	16,000	5300	4350
Storage volume for 10^6 kJ, avg	[m^3]	26.8	16	6.6	2.7
Relative storage mass		13.79	4	1.25	1.0
Relative storage volume		10	6	2.5	1.0

1. Storage mass and volume are calculated for storing 106 kJ energy with a temperature rise of 15 K for concrete (sand and gravel) and water.
2. Relative mass and volume are based on the inorganic phase change materials.

The experimental approaches offer a better indication of the actual PCM behavior and performance in comparison to theoretical analysis, as the experimental tests can present the PCMs' behaviors more directly, visibly and credibly without any pre-set assumptions however, the experiments are unachievable in some cases, such as the large scale or unsteady around environment, so there are still a few points need to be considered:

- Time and cost consuming will be higher than a theoretical approach, hence, the budget and processes needs to be established and scheduled.
- The scales of the experiment test rig have to be considered, and then suitable laboratory location and space needs to be determined to house the rig.
- Test rig needs to be constructed and operated properly.
- Proper environment parameters have to be simulated and adjusted to imitate the practical environment.
- Relevant parameters need to be monitored, measuring apparatuses need to be calibrated, and the failed data need to be eliminated.

Except these agonizing experimental matters, there are still some unavoidable testing errors. However the theoretical methods can avoid all these weakness and predicate the PCMs performance conveniently. The major advantage of the theoretical/numerical approaches is that various conditions can be carried out by changing the variables in a numerical model. Therefore, more and more investigators prefer to study the phase change problems by mathematical solutions and numerical simulations. There are only eight review papers on PCMs that involves the aspect of mathematical solutions and/or numerical modeling of latent heat thermal energy storage (LHTES) have been published during 2002–2012. Table 2 summaries these eight relative review papers and comments their mathematical and/or numerical aspects of LHTES. However, few logistic and comprehensive reviews on the mathematical solutions and numerical modeling for melting and solidification processes of PCMs were found in published literatures even though there are many individual publications in phase change problems, particularly in heat transfer mechanisms and simulations. Due to the complexity of phase transformations,

Table 2
Some review papers related to numerical study of phase change problems.

Reference	Published year	Journal	Comment
Zalba et al. [1]	2003	Applied thermal engineering	The review was divided into three parts: materials, heat transfer and applications. Heat transfer was considered mainly from a theoretical point of view, considering different simulation techniques.
Verma et al. [2]	2008	Renewable and sustainable energy reviews	Mathematical models of a LHTES were reviewed to optimize the material selection and to assist in the optimal designing of the systems. Some important characteristics of different models and their assumptions used were presented and discussed as well.
Jegadheeswaran and Pohekar [3]	2009	Renewable and sustainable energy reviews	Various thermal conductivity enhancement techniques reviewed in this paper, and the issues related to mathematical modeling of LHTES with enhancement techniques are also discussed.
Zhu et al. [4]	2009	Energy conversion and management	This paper presented an overview on dynamic characteristics and energy performance of buildings employing PCMs by three research methods used, i.e., simulation, experiment, combined simulation and experiment
Agyenim et al. [5]	2010	Renewable and sustainable energy reviews	This paper provided the formulation of the phase change problem. In terms of problem formulation, it was concluded that the common approach has been the use of enthalpy formulation.
Kuznik [6]	2011	Renewable and sustainable energy reviews	The review was the first comprehensive review of the integration of phase change materials in building walls. Various numerical studies concerning the integration were summarized.
Dutil et al. [7]	2011	Renewable and sustainable energy reviews	The review presented models based on the first law and on the second law of thermodynamics. This paper tried to enable one to start his/her research with an exhaustive overview of the subject.
Zhou [8]	2012	Applied energy	This paper reviewed previous works on latent thermal energy storage in building applications, including PCMs, current building applications and their thermal performance analyses, as well as numerical simulation of buildings with PCMs.

a good understanding of the heat transfer mechanisms, phase change characteristics and the differences among various mathematical and numerical simulation methods is required before researchers starting their theoretical study. The aim of this paper is to comprehensively study the mathematical and simulation modeling applied for LHTES. Firstly it discusses the issues of the heat transfer mechanisms during the charging and discharging processes and the Stephan problem and Neumann problem. Secondly, it sums the strong and weak aspects of various mathematical solutions when conduction and convection heat transfer occurring inside the PCMs by the considering fixed grid method and the adaptive grid method. Finally, numerical modeling of various PCM packages' geometries in terms of macro-encapsulated PCMs and micro-encapsulated PCMs are studied.

2. Heat transfer mechanisms during the phase transformations

2.1. Conduction and convection heat transfer

During the charging and discharging processes, the possible heat transfer mechanisms are conduction and convection. However, the issue of which heat transfers mechanism takes the main role in different stages of phase transformation has been argued for decades. When PCMs are used to store or release thermal energy, conduction is usually believed playing the most important role on the heat transfer during the phase transformation processes [2–4]. As early as 1831, Lamé and Clapeyron have conducted the first study on phase change problem by only considering the pure conduction. However, some researchers persist that natural convection is a more important mechanism in the phase change process especially in the melt region. Lazaridis [100] proposed a study of the relative importance of conduction and convection in 1970. A pioneer study performed by Sparrow et al. in 1977 [41], they concluded in their study that natural convection could not be ignored in the analysis of phase change problems. In 1994, Hasan [5] concluded that the convection heat transfer active an important role in the melting process, and a simplified model by only considering the conduction heat transfer does not describe the melting process properly. Later, Lacroix et al. [6] reported the similar findings in their research that natural convection is the main heat transfer mechanism during the melting process. In 1999, Velraj [7] obtained the same conclusion in their research and reported that during the melting process natural convection occurs in the melt layer which results in the heat transfer rate increase comparing to the solidification process. Buddhi et al. [8] proposed an explanation for this phenomenon that the density differences between the solid and liquid PCM induce the buoyancy, which causes the convective motions in the liquid phase. However, Zhang and Yi [9] believed that with the solid PCM melting into liquid, the PCM volume keeps increasing, which results in the convection becoming the predominant heat transfer mechanism rather than conduction. Sari et al. [10] found that the heat transferred from a heat exchanger to a PCM of stearic acid is largely influenced by natural convection at the melting layer, in addition to conduction and forced convection heat transfer.

For the melting process, the PCM changes its phase from solid to a mushy state, and then liquid, which is reversible during the solidification process. Hence there are six stages to finish a charging and discharging cycle. Therefore it is possible in certain stages of the phase transformation process there are more than one kind of heat transfer mechanisms acting at work, but how to weight the percentages of conduction and convection heat transfer in each stage has been the main challenge for the researchers currently. This paper will review the most common research methods used for the conduction and convection heat transfer inside the PCM packages.

2.2. Stefan problem

Moving boundary problem named Stefan problem is another issue to develop a numerical modeling of PCMs [11,12]. The simplest of the Stefan problems is the one-phase Stefan problem since only one-phase involved. The term of 'one-phase' designates only the liquid phases active in the transformation and the solid phase stay at its melting temperature. Stefan's solution with constant thermophysical properties shows that the rate of melting or solidification in a semi-infinite region is governed by a dimensionless number, known as the Stefan number (St),

$$St = \frac{[C_l(T_l - T_m)]}{L} \quad (1)$$

where C_l is the heat capacity of the liquid PCMs, L is the latent heat of fusion, and T_l and T_m are the surrounding and melting temperatures, respectively.

The most published solutions are to solve the one-dimensional cases subjected to an infinite or semi-infinite region with simple initial and boundary conditions. Whereas with the heat transfer continuing, the interface boundary is constantly moving as the liquid and solid phases shrinking and growing, which disable the prediction of the boundary location [13]. Because of that the solid–liquid interface is not fixed, but moving with time, the heat transfer mechanisms during a PCM phase transformation process are complex. Therefore the phase change transition is difficult to analyze owing to the three reasons: the solid–liquid interface is moving; the interface location is non linear; it consists of thermal conduction and natural convection heat transfer mechanisms. Since these three factors, the non-linearity of the governing equations is introduced to the moving boundary, and the precise analytical solutions are only possible for a limited number of scenarios [14]. This view is shared by Kürklü et al. [15] who pointed out that the mathematical models have been proposed in each research only applied to very specific boundary conditions, hence are not feasible to more complex practical applications. This Stefan problem is further complicated by the fact that most of the methods previously proposed by researchers only involve one moving boundary, whereas it actually consist of more than one interface location [16].

2.3. Neumann problem

The Stefan problem was extended to the two-phase problem, the so-called Neumann problem which is more realistic [17]. In Neumann problem, the initial state of the PCM is assumed to be solid, during the melting process, its initial temperature does not equal to the phase change temperature, and the melting temperature does not maintain at a constant value. If the melting happens in a semi-infinite slab ($0 < x < \infty$), the solid PCM is initially at a uniform temperature ($T_s < T_m$), and a constant temperature (T_0) is imposed on the slab surface $x = 0$, with the assumptions of constant thermo-physical properties of the PCM, the problem can be mathematically expressed as follows:

Heat conduction in solid or liquid region

$$\rho C \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} \tag{2}$$

where ρ is the density, C is the specific heat, k is the thermal conductivity, and t and x are the time and space coordinates respectively.

The heat fluxes transferring from the liquid phase to the solid–liquid interface, as well as the latent heat absorbing rate by the melting PCM, the movement of the solid/liquid interface can be determined through the following energy balance:

$$\rho L \frac{\partial x_t}{\partial t} = -k_l \frac{\partial T_l}{\partial x} + k_s \frac{\partial T_s}{\partial x} \tag{3}$$

where L is the latent heat of fusion of the PCM and ρ is the density of liquid PCM.

Initial condition

$$T(x > 0, t = 0) = T_s < T_m \tag{4}$$

Solid–liquid interface temperature

$$T(x = \delta(t),\ t > 0) = T_m \tag{5}$$

With the following boundary conditions:

$$T(0,\ t) = T_0 > T_m \quad \text{for } t > 0 \tag{6}$$

$$T(x,\ t) = T_s \quad \text{for } x \to \infty,\ t > 0 \tag{7}$$

where $\delta(t)$ is the position of the solid–liquid interface (melting front). Fig. 1 clearly illustrates this two-phase Stefan problem.

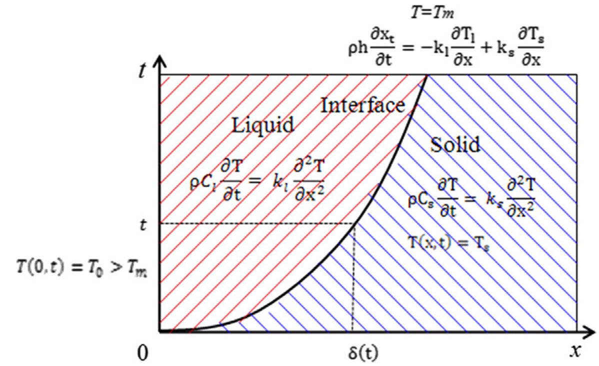


Fig. 1. Schematic illustration of the two-phase Stefan problem.

Analytical solution to such a problem was obtained by Neumann in term of a similarity variable η

$$\eta = \frac{\delta(t)}{2\sqrt{\propto_l}} \tag{8}$$

The final Neumann's solution can be written as

Interface position

$$\delta(t) = 2\lambda\sqrt{\propto_l t} \tag{9}$$

Temperature of the liquid phase

$$T(x,t) = T_l - (T_l - T_m)\frac{erf(x/2\sqrt{\propto_l t})}{erf(\lambda)} \tag{10}$$

Temperature of the solid phase

$$T(x,t) = T_s + (T_m - T_s)\frac{erfc(x/2\sqrt{\propto_s t})}{erfc(\lambda\sqrt{\propto_l/\propto_s})} \tag{11}$$

The λ in Eq. (9)–(11) is the solution to the transcendental equation

$$\frac{St_l}{\exp(\lambda^2)erf(\lambda)} - \frac{St_s\sqrt{\propto_s}}{\sqrt{\propto_l}\exp(\propto_l\lambda^2/\propto_s)erfc(\lambda\sqrt{\propto_l/\propto_s})} = \lambda\sqrt{\pi} \tag{12}$$

where

$$St_l = \frac{C_l(T_l - T_m)}{L} \tag{13}$$

$$St_s = \frac{C_s(T_m - T_s)}{L} \tag{14}$$

However, the Neumann's solution is applicable only for moving boundary problems in the rectangular coordinate system.

2.4. Other possibility mechanisms in phase change process

Furthermore, there are several other issues with the use of a theoretical approach in the study of PCMs. Alexiades [18] pointed out that there were many mechanisms involved during a PCM phase transition, such like a change in volume, density, thermal conductivity, specific heat capacity, super-cooling, etc. Consequently, accurate reflection of the proposed mathematical solution and numerical model need to consider the dynamic properties of the phase change process. Another major issue with PCMs is that they act as self-insulating materials. When PCM solidification occurs from the top of the heat surface, solid insulating layer will be developed which moves inward during the whole solidification process. With the increase in the size and thickness of the solid layer, the heat transfer rate from the liquid PCM to the heat exchanger surface decreases until it becomes so small that will not

be possible to maintain at an acceptable heat transfer rate. The self-insulating characteristic of the PCM becomes a strong problem when bulk containerization is used. For example the large cylindrical used as containers filled with PCM, the self-insulating issue can become very serious. Large heat exchange area will accelerate the formation of the crust and heavily decrease the heat transfer rate. Radhakrishnan et al. [14] analyzed that the method to lighten the crust issue is minimizing the depth of the PCM pack. So that even a large majority of the PCM performs solidification, the thermal resistance is reduced to allow the removal of the latent heat released from the solidified PCM. The self-insulating characteristic of the PCM during discharging process needs to be considered in any mathematical model as this can affect thermal energy discharging time and rate. Furthermore, the self-insulating has a direct effect on the phase transition boundary, where the solid and liquid region meets and co-exists, which is linked back to the Stephan Problem and Neumann's method again.

Logical heat transfer mechanisms during the charging and discharging periods of the PCM are the essential elements to develop any accurate mathematical model. However, as described there are quite a few issues to properly describe the heat transfer mechanisms: conduction and natural convention during the phase change process. This paper reviews most of the researches employing the mathematical calculation and numerical simulation published in the articles and reports, but does not find any consensuses on which one is the dominant heat transfer mechanism, which one can be ignored and how to combine these two transfer mechanisms in each modeling. Different researchers have developed their specific methods to evaluate the thermal energy transfer during the phase transition process for various situations [19–23].

3. Mathematical solutions

The analyzes of the heat transfer mechanisms in phase change processes are complex owing to the movable solid–liquid boundary, which depends on the latent heat absorbing or releasing rate at the interface. In order to simplify the simulation of the phase change problems, assumptions have been made by various researchers in their studies. In this section, different numerical simulations in terms of conduction heat transfer and conduction and/or convection heat transfer are discussed and analyzed.

3.1. Conduction acting as the only heat transfer mechanism

To develop a mathematical model, the dominant heat transfer mechanism whether conduction or convection, during the charging and discharging processes, need to be analyzed and determined. Although there are quite a few issues in the heat transfer mechanisms during the phase transformation, some researchers simplify this process by only considering conduction in pure substances. In this case, the mathematical solutions can be classified as follows: fixed grid and adaptive grid.

3.1.1. Fixed grid

Fixed grid method does not require explicit treatment of conditions on the phase change boundary, and just requires the use of fixed-grid schemes able to cope with strong nonlinearities. Therefore this method is able to utilize standard solution procedures for the energy equations. They are amenable to physical interpretation and easy to implement, especially for multidimensional problems and for mufti-interface problems.

In the fixed grid method, the heat flow equation is approximated by finite difference replacements for the derivatives in order to calculate the values of temperature $T_{i,j}$, at any time $t_n = n\Delta t$, the

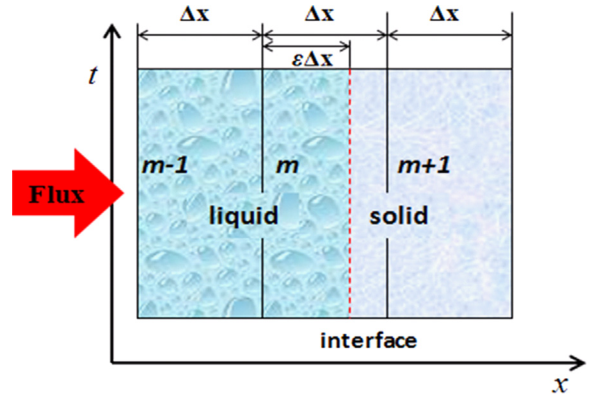


Fig. 2. Position of the moving boundary in a fixed grid.

moving boundary will be located between two adjacent grid points, for instance, between $m\Delta x$ and $(m+1)\Delta x$ (at a location of $\varepsilon\Delta x$, where $0<\varepsilon<1$), as illustrated in Fig. 2.

The mathematical solution of the one-phase ice-melting presents a simple illustration of this method. The instantaneous temperature at point $(i,j+1)$ is calculated from the temperatures of the previous step on the basis of the following formulation:

$$T_{i,j+1} = T_{i,j} + \left(\frac{\Delta t}{\Delta x^2}\right)(T_{i-1,j} - 2T_{i,j} + T_{i+1,j}) \quad i = 0, 1, \ldots m-1. \tag{15}$$

In terms of three-point Lagrange interpolation instead of Eq. (14), the temperature at $x = m\Delta x$ is computed as,

$$T_{m,n+1} = T_{m,n} + \left(\frac{2\Delta t}{\Delta x^2}\right)\left(\frac{1}{\varepsilon_{n+1}}T_{m-1,n} - \frac{1}{\varepsilon_n}T_{m,n}\right) \tag{16}$$

The variation of the location of the moving boundary is

$$\varepsilon_{n+1} = \varepsilon_n - \left(\frac{\Delta t}{\Delta x^2}\right)\left(\frac{\varepsilon_n}{\varepsilon_{n+1}}T_{m-1,n} - \frac{1}{\varepsilon_n}T_{m,n}\right) \tag{17}$$

As shown, the numerical solution of this fixed grid method is carried out on a space grid remaining at a fixed value throughout the mathematical calculation. To approximate the Stefan conditions both for the moving boundary and the partial differential equation at the adjacent grid points, various mathematical solutions have been proposed. Murray and Landis [24] proposed two fictitious temperatures: one is achieved by quadratic extrapolation from the temperatures in the solid PCM and the other one is from the temperatures in the liquid PCM. The melting temperature and the position of the moving interface are incorporated in the fictitious temperatures, which are then substituted into a standard approximate to calculate the temperature near the interface instead of using special formulae. Ciment and Guenther [25] introduced a method of spatial mesh refinement on both sides of the moving boundary. With this method, Lazaridis [26] applied the explicit finite difference approximations to solve two-phase solidification problems in both two and three space dimensions.

The major advantage of the fixed grid method is that the mathematical calculation of the phase transition can be achieved through simple modifications of existing heat transfer numerical methods and/or software. As such, they can be used for modeling of a variety of complex moving boundary problems. Basu and Date [27] and Voller et al. [28] reviewed the applications of the fixed grid methods for phase change problem. The two mainly fixed-grid methods that have been proposed are enthalpy-based methods and the effective heat capacity method. However, the fixed grid method sometimes cannot work efficiently when the boundary

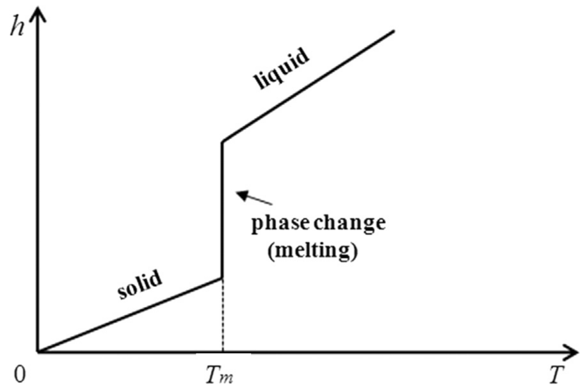


Fig. 3. Relationships between enthalpy and temperature for isothermal phase change.

moves along a distance larger than a space increment in a time step, depending on the velocity of the moving boundary. Therefore, the adaptive grid is developed by researchers and will be discussed in Section 3.1.2.

3.1.1.1. Enthalpy based method. The existence of nonlinearity of the liquid–solid interface and the unknown location of the moving boundary are the two main challenges in simulating the phase change problems [29]. To deal with these, a new model formulation called the enthalpy method was introduced [30]. In the enthalpy models, the enthalpy is used as a dependent variable value along with temperature. By introducing an enthalpy method, the phase-change problem becomes much easier since the governing equations are the same for the two phases. The interface conditions are automatically achieved and a mushy zone between the two phases is created. This zone avoids sharp discontinuities that may create some numerical instability. Hence, the enthalpy mathematical methods are most attractive and commonly used to handle phase change problems where a solid–liquid mush zone is present between two phases. Hunter [31] confirmed that the enthalpy method is most suitable for typical applications, the reason for that is this method does not require explicit treatment of the conditions on the phase change boundary [32].

Enthalpy-based method can be illustrated by considering a one-dimensional heat conduction controlled phase transformation. For a phase change process, energy conservation can be expressed in terms of total volumetric enthalpy and temperature. This relationship between the enthalpy and temperature is usually assumed to be a step function for isothermal phase change problems. Fig. 3 shows the enthalpy–temperature curves for isothermal phase change.

For isothermal phase change, the conservation of energy can be expressed in terms of temperature and the total volumetric enthalpy [33]

$$\frac{\partial H}{\partial t} = \nabla[k(\nabla T)] \tag{18}$$

where the total volumetric enthalpy H is the sum of sensible and latent heat, and can be expressed in terms of temperature of the PCM as follows:

$$H(T) = \Delta H(T) + \rho_l f(T)\lambda \tag{19}$$

The first term on the right side of Eq. (19) accounts for the sensible heat of the PCM while the second term accounts for the latent heat of the PCM.

And where

$$\Delta H = \int_{T_m}^{T} \rho c dT \tag{20}$$

To be able to calculate the total enthalpy, the liquid fraction λ is given as follows:

$$\lambda = \begin{cases} 0 & T < T_m \quad \text{solid} \\ ]0,1[& T = T_m \quad \text{mushy} \\ 1 & T > T_m \quad \text{liquid} \end{cases} \tag{21}$$

Integrating the Eqs. (18) and (20), an alternate form for one-dimensional heat transfer in the PCM was obtained:

$$\frac{\partial \Delta H}{\partial t} = \frac{\partial}{\partial x}\left(\alpha \frac{\partial \Delta H}{\partial x}\right) - \rho_l \lambda \frac{\partial f}{\partial t} \tag{22}$$

where α is the thermal diffusivity.

3.1.1.2. Effective heat capacity method (energy based method). The effective heat capacity method is also a common method used in modeling phase change problems except for the enthalpy method. The effective heat capacity method was first proposed in [34,35]. In the effective heat capacity method, the latent heat is approximated by a large heat insensible form over the phase change temperature interval, $(T_2 - T_1)$ [36]. The effective heat capacity of the PCM (c_{eff}) is directly proportional to the energy stored and released during the phase change but inversely proportional to the interval of the melting or solidification temperature range. During the phase change the heat capacity of the PCM is

$$c_{eff} = \frac{L}{T_2 - T_1} + c_s \tag{23}$$

where T_1 is the temperature at which melting or solidification begins and T_2 is the temperature at which the PCM is totally melted or solidified. The following is a definition of the effective heat capacity for each phase change period.

$$c_{eff} = \begin{cases} c_s & T < T_1 \quad \text{solid} \\ \frac{L}{T_2 - T_1} + c_s & T_1 \le T \le T_2 \quad \text{mushy} \\ c_l & T > T_2 \quad \text{liquid} \end{cases} \tag{24}$$

In terms of the definition of the effective heat capacity, the energy equation for one dimension can be written as follows:

$$\rho c_{eff} \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} \tag{25}$$

Although the enthalpy based method and the effective heat capacity method achieve much simpler mathematical operations with reasonable accuracy, it is worth noting that each of the methods has its inherent disadvantages. Enthalpy method is difficult to handle super-cooling and temperature oscillation problems. Whilst the effective heat capacity method is difficult in resolving the phase change problems when the phase change temperature range is small, and is not applicable for the cases where phase change occurs at fixed temperature.

Two approaches, finite-difference and finite-element techniques, are firstly used to solve the phase change problems numerically. The first finite-difference studies were carried out by Lamé and Clapeyron in 1831 and Stefan in 1891, concerning ice formation. In 1912 the results of Neuman were published, establishing the precise solutions to more general phase change problems. In 1943, London and Seban [37] analyzed the process of ice formation for different geometries (cylinder, sphere, and flat plate). However, Shamsundar

and Srinivasan [38] asserted that London's one-dimensional formulation led to errors by increasing the progress of the solidification process and proposed a two-dimensional formulation for cylinders. A one-dimensional formulation was presented by Bonacina et al. to assess the accuracy of the effective heat capacity method [39]. Rabin and Korin presented a multidimensional numerical solution based on the effective heat capacity method for solving transient phase change problems by using the finite-difference method [40]. The proposed mathematical method showed a good agreement with two exact solutions and two numerical solutions based on finite-difference and finite-element methods.

Although the finite-difference method has been traditionally employed for solving phase change problems in the past, oscillations in the front position and/or temperature occur due to a poor heat balance when the phase change front lies between nodes in a finite difference solution [41,42]. Nowadays the finite-element method has been more attractive, because of the ability of the finite-element method to handle complex coupled thermomechanical mechanisms with various and complex boundary conditions [43]. Consequently, finite-element methods can either accurately represent the temperature history or track the phase front, or both. A few earlier studies based on finite-element formulations were carried out by Rubinsky and Cravahlo in 1981 [44] and Ettouney and Brown in 1982 [45], concerning on the location of the solid–liquid interface. To deal with oscillations, Comini et al. [46] and McAdie et al. [47] developed finite-element based enthalpy formulations, and applied the three level Predictor–Corrector and Regula-Falsi methods to account for the sudden jumps or sharp changes in the enthalpy–temperature relationships. Bhattacharya et al. developed a new enthalpy based method to study phase change in a multicomponent material using the Galerkin finite-element method. This method can efficiently capture multiple thawing fronts which may originate at any spatial location within the sample [48]. Hence, finite-element methods are preferred to be used in enthalpy approaches and the effective heat capacity method.

Beside the finite-difference and finite-element methods, the finite-volume and control-volume- finite-element methods were also employed to handle the phase change problems [39].

3.1.2. Adaptive grid

The problem associated with the fixed grid method can be deal with by utilizing the adaptive grid method to improve the computational efficiency, using the so-called adaptive grid (or front tracking) numerical schemes to capture the moving boundary [49]. In the adaptive grid method, the exact location of the moving boundary is evaluated on a grid at each step. There are two main approaches used to achieve this: the interface-fitting grids and the variable-space grids. The interface-fitting grids (also referred to as the variable time step methods), where a uniform spatial grid but a non-uniform time step are used, has been repeatedly employed to solve two-phase and one-dimensional problems. The another approach is variable-space grids, also known as the dynamic grids, where the number of spatial intervals is kept constant and the spatial intervals are adjusted in such a manner so that the moving boundary lies on a particular grid point. Thus, in these methods the spatial intervals are a function of time. The applications of the variable grid method to study the phase change problem can be found in [50–54].

Lacroix and Voller [55] performed a study on simulation of diffusion/convection controlled solidification processes in a rectangular cavity by using the finite-difference techniques. They concluded that the fixed grid must be finer for solving the melting problem of a material with a unique melting temperature. Comparison between the fixed and adaptive grid has also been done by Bertrand et al. [56]. They found that the adaptive grid method is better adapted to the melting problem than the fixed grid method. However the adaptive grid method may fail to simulate the situations where the transition from the liquid to the solid phase is not a macroscopic surface.

Table 3 presents some references of the mathematical and numerical studies undertaken with the only consideration of the conduction heat transfer.

3.2. Conduction and convection heat transfer mechanisms

During the phase transformation especially melting process, the temperature and concentration gradients in the liquid phase of PCM keep varying, which results in the movement of the liquid PCM, named convection occurring under the action of buoyancy forces due to the density gradients. In the previous numerical investigations, the convection heat flow in the liquid phase received less attention than conduction owing to the limited computational capabilities of computer and the mathematical complexities to formulate the convection heat transfer during the phase transformation. The influence of the natural convection on the phase change problems were initially considered in 1977. The study of the possible role of the natural convection in the melt region has been conducted by Sparrow et al. in 1978 [67]. The findings of this study indicated that the natural convection is first-order important and has to be accounted in the phase transformation analysis. A number of researchers [68–71] have also reported that the convection affects not only the rate of melting or solidification but also the resulting of the distribution of the liquid phase of the PCM in a multi-component system. One of the pioneer numerical studies was carried out by Yao and Chen in 1980 [72], by using an approximate solution. They studied the effect of the natural convection on the phase change process and concluded that it strongly depends on the Rayleigh number. The equation of $k_e/k_l = cRa^n$ includes an effective of thermal conductivity was used to describe the influence of natural convection on the melting process [73,74].

The influence of the convection heat transfer on the melting and freezing processes has been studied by Lamberg et al. [64], they found that when the effect of natural convection is omitted in the simulation. The numerical result was poor compared with the experimental result during the melting process, whilst it showed a good estimation during the freezing process. Hence it is essential to model natural convection in the liquid PCM during the melting process. Besides the numerical methods mentioned in Section 3.1, the integral method [75], boundary fixing method [76], unstructured finite-element method [77], enthalpy-porosity approach [78–80], coordinate transformation method [81,82] and equivalent thermal capacity method [83] have been developed for natural convection simulation.

Yao and Cherney [84] studied the effect of the natural convection on the melting of a solid PCM around a hot horizontal cylinder by using the integral method. The results demonstrated that the integral solution had surprising accuracy when it was compared with the quasi-steady solution when Stefan number was small. Rieger et al. [85] investigated numerically the melting process of a PCM inside a heated horizontal circular cylinder. Both heat conduction and convection have been taken into account to treat this moving boundary problem, and the complex structure of the time-wise changing physical domain (melt region) have been successfully overcome by applying body fitted coordinate technique. Ismail and Silva [86] developed a 2D mathematical model to study the melting of a PCM around a horizontal circular cylinder considering the presence of the natural convection in the melt region. A coordinate transformation technique was used to fix the moving front. The numerical predictions were compared with available results to establish the validity of the model, and a

Table 3
Numerical studies by only considering the conduction heat transfer.

Reference(s)	Dimensional	Numerical simulation method	Assumptions	Comment	Validation
Silva et al. [57]	1D	Enthalpy based method	• 1-D conduction controlled the phase change process. • The fluid flow was fully developed with temperature independent properties. • Thermal radiation between the wall and fluid was neglected.	The model can be used to predict the dynamic performance of this kind of vertical rectangular heat exchange unit with reasonable accuracy	Yes
Kürklü et al. [15]	2D	Energy based equation	• The phases were homogeneous. • Conduction heat transfer was only considered. • Heat loss or gain from the store was neglected.	Calculating the temperature of air and PCM at the formerly defined volume nodes.	Yes
Costa et al. [3]	2D	Energy based equation. Fully implicit finite-difference method.	• The thermophysical properties of the PCM and fin were independent of temperature. • The PCM was initially in the solid phase. • The PCM was homogenous and isotropic.	Calculations have been made for the melt fraction and energy is stored by conduction only	Numerical [33,58]
Gong et al. [59]	2D	Enthalpy based method. Standard Galerkin finite-element	• The heat-transfer fluid was incompressible and viscous dissipation was negligible. • The fluid flow was radially uniform and the axial velocity was an independent parameter. • Thermal losses through the outer wall of the PCM were negligible. • Conduction heat transfer was the mainly transfer method.	For mode1, simulation has been done by introducing hot and cold fluids from the same end of the tube. While for mode 2, simulation has been done by introducing hot and cold fluids from the different ends of the tube.	No
Sharma et al. [60]	2D	Enthalpy based method Fully implicit finite-difference method	• The thermo-physical properties of PCM's and fin material were independent of temperature but different for solid and liquid phases. • The PCM was initially in solid phase. The PCM was homogeneous and isotropic. • The mode of heat transfer was conduction only.	Calculations were made to study the effect of thermal conductivity and thermal capacity of fatty acids, and conductivity of heat exchanger materials and their effect on melt fraction.	No
Dwarka and Kim [61]	3D	Implicit enthalpy based method.	• Air temperature was constant. • Initial temperatures were the same through the board. • There was no energy loss to surroundings. Conduction heat transfer was only considered. • All thermo-physical properties were constant except for the heat capacity.	Comparison of the thermal performance of randomly mixed and laminated PCM drywall system	No
Dolado et al. [62]	1D	Finite-difference method	• Only conduction heat transfer was considered inside the PCM plate. • The temperature of the airflow was analyzed in a one dimensional way.	A model was developed to simulate the performance of a LHTES, and analyze the heat transfer between the air and a commercial macroencapsulated PCM.	Yes
Fukai et al. [63]	2D	Enthalpy based method Control-volume method	• The surfaces of the heat exchanger were adiabatic. • The cross-sections of the tubes was square • The convective heat transfer term was neglected.	A numerical model predicted well the experimental outlet fluid temperatures and the local temperatures in the composite.	Yes
Lamberg et al. [64]	2D	Enthalpy based method and Effective heat capacity method	• The heat conductivity and density of the PCM and container were constant. • The physical properties chosen for the PCM were the average values of solid and liquid PCM. • The convection heat transfer was negligible during solidification process.	Both numerical methods gave good estimations for the temperature distribution. Particularly, when the temperature range was 2 °C, the effective heat capacity method was the most precise numerical method.	Yes
Zivkovic and Fujii [65]	1D	Enthalpy based method	• The effects of natural convection within the melt were negligible and can be ignored. • The PCM behaved ideally. • The PCM was assumed to have a definite melting temperature.	The cylindrical container required nearly twice of the melting time as for the rectangular container of the same volume and heat transfer area	Yes

Table 3 (*continued*)

Reference(s)	Dimensional	Numerical simulation method	Assumptions	Comment	Validation
Saman et al. [66]	2D	Enthalpy based equation	• The thermo physical properties of PCM can be assumed constant. • The PCM was initially solid and its temperature was assumed at a certain value below the melting point. • The natural convection was taken into account during charging period.	The numerical model was able to predict quite accurately the melting time and the heat transfer rate during the melting with the geometry being considered	Yes

satisfactory agreement was found. They concluded that the numerical model was adequate to represent the physical situation of the proposed system.

Furzerland [87] investigated the enthalpy method and the coordinate transformation method through the comparison of the solutions of specific problems of one dimensional heat transfer by considering pure convection. One of his conclusions was that the enthalpy method is very attractive owing to these: it is easy to program and there are no computational overheads associated with tracking the moving interface within a specific range of fusion temperatures.

A summary for various numerical solutions on phase change problem considering both conduction and convection is presented in Table 4.

4. Numerical models for various PCMs capsules and packages

It can be easily found that solid–liquid PCMs have been widely used for studies on phase change problems compared to solid–solid, liquid–gas and solid–gas PCMs. This is due to their large heat storage capacity and little volume change during the phase change process. Since solid–liquid PCMs experience a phase transition during the charging process and/or charging process, encapsulation is required for holding the liquid and/or solid phases of the PCM and keeping it isolate from the surrounding. This ensures the flexibility in frequent phase change processes, and an increase in heat transfer rate. It is worth noting that the heat transfer characteristics in the encapsulated PCM would change significantly depending on the parameters of various encapsulations. Hence, vast of numerical studies on phase change problems have extended to engineering applications. In this section, a comprehensive review on numerical models for encapsulated PCMs in terms of macro-encapsulated PCM and microencapsulated PCM is presented.

4.1. Macro-encapsulated PCMs numerical models

Macro-encapsulation is a common form of encapsulation used for thermal storage applications. The shape of macro-encapsulate varies from rectangular panels, spheres to cylinders.

4.1.1. Rectangular encapsulation

The most intensely investigated LHS containment is the rectangular encapsulation because to its simple boundary conditions and easy work principle. The first numerical study on rectangular geometry has been conducted by Shamsundar and Sparrow [107,108] in 1975 and 1976 by applying the finite-difference method to investigate the solidification of a flat plate. Shamsundar also used the same method to the case of a square geometry [109] in 1978.

Hamdan and Elwerr [110] presented a simple 2-D numerical model to study the melting process of a solid PCM within a rectangular enclosure. In this model, the rate of melting depends essentially on the properties of the PCM, such as the thermal diffusivity, viscosity, conductivity, latent heat of fusion and specific heat. Natural convection was treated as the dominant heat transfer mode within the melt region. Conduction was only assumed to take place within the layer very close to the solid boundary. The numerical results showed a high agreement with previously published experimental results [111,112]. Therefore, it can be effectively used to predict the energy storage performance of the PCMs contained within the rectangular encapsulation.

Further research was carried out by Lacroix [113] in 2001, who presented a mathematical model based on the energy conservation equation to study the contact melting of a sub-cooled PCM inside a rectangular cavity including the natural convection effect. Numerical results demonstrated that the melted fraction at the bottom of the cavity is larger, by an order of magnitude than that of the conduction dominated melting at the top. The melting process is essentially governed by the magnitude of the Stefan number and strongly influenced by the lateral dimensions of the cavity. Jiji and Gaye [114] also analytically examined one-dimensional solidification and melting of a slab with uniform volumetric energy generation. They found that the low thermal conductivity of the PCMs present a significant challenge in the design of PCM-based electronic cooling systems.

In order to address the inherent drawback of the low thermal conductivity of PCM, various numerical solutions have been applied for PCM with different thermal conductivity enhancers (TCEs). Lacroix and Benmadda [115] numerically analyzed the melting of PCMs in a rectangular enclosure with horizontal fins. A 2-D enthalpy model was used to solve the phase change problem using a fixed-gird method. The effects of the number and length of fins on the melting rate were considered in this study. It was concluded that a few longer fins were more effective in the melting rate than a large number of shorter fins. The effect of vertical fins on melting rate was studied by the same team [116] by using a fixed-grid enthalpy model in 1998. It was found that the onset of natural convection in the melted zone was delayed when the distance between the fins was decreased. According to their results, the optimum fin spacing decreases as the Rayleigh number increases. Akhilesh et al. [117] numerically studied a rectangular module with vertical fins, which was heated from above. The numerical model was solved by using finite-difference method. Only conduction heat transfer was included in this study. The analysis showed that more fins increase the rate of energy stored in the melting PCM until a critical value. There is no obvious performance enhancement by only increasing the number of fins beyond the value. Similar results were obtained in another research of Gharebagi and Sezai [118] in 2005 considering an enclosure with vertical fins added to a horizontal heated wall. The results indicated that the heat transfer rate to the melting PCM can be improved by adding fins. In addition, vertically heated walls with horizontal fins exhibit better performance than horizontally heated walls with vertical fins.

Table 4
Numerical studies by considering both the conduction and convection.

Reference(s)	Dimensional	Numerical solution method	Assumptions	Comment	Validation
Costa et al. [3]	1D	Energy based equation Fully implicit finite-difference method	• The thermophysical properties of the PCM and fin material were independent of temperature. • The PCM was initially in the solid phase. • The PCM was homogenous and isotropic.	Calculations have been made for the melt fraction and energy stored under conduction plus convection condition.	Numerical [30,58]
Halawa et al. [88]	2D	Enthalpy based method	• For the PCM melting process, the PCM was solid and its temperature was assumed at a certain value below the melting point. • For freezing process, the PCM was initially liquid and its temperature was assumed at certain value above the melting point.	Typical characteristics of the melting/freezing of PCM slabs were discussed. Considerations in the design of the LHTES were also given.	Numerical [89]
Wang et al. [90]	2D	Energy based method Finite-volume method	• The PCM was pure and homogeneous. • The melting front was an isothermal interface in reality. • The thermophysical properties of the PCM were constant, with the exception of the linear density–temperature relation. • The natural convection flow of the liquid phase was incompressible and laminar with no viscous dissipation. • The density of PCM was constant in this study.	Calculations were performed to study the effect of thermal conductivity and thermal capacity of fatty acids and conductivity of heat exchanger materials and their effect on melt fraction.	No
Jana [91]	2D	Enthalpy-porosity based method Finite-volume method	• The density was considered to be constant in the unsteady and convective terms and was allowed to vary only in the body-force term, • The phase change occurred at a single temperature, • The temperatures of liquid and solid at the interface were equal.	Prediction of solidification and melting processes of pure materials using moving grids.	Numerical and Experimental [92]
Hamdan and Al-Hinti [93]	3D	–	• The solid–liquid interface was smooth, plane. • The solid phase was initially at the melting temperature. • The effect of inertia inside the thermal boundary layers was negligible relative to that of buoyancy and viscosity. • The heat loss from the walls of the enclosure was negligible. • The PCM material was pure, homogenous and isotropic. • Boussinesq approximation was used in this analysis.	The melting process of a solid PCM contained in a rectangular enclosure heated from a vertical side at a constant heat flux was investigated analytically.	Experimental [94]
Zhao et al. [95]	1D	Energy based equation	• The heat transfer process inside the molten layer was one-dimensional, and the tangential temperature gradient was neglected. • The thermo-physical properties of PCM were constant. • The process was quasi-steady, and the acting forces on PCM were balanced at every moment of the melting.	The expression of melting velocity was obtained by using the lubrication theory.	Numerical and Experimental [96]
Liu et al. [97]	2D 3D	Enthalpy porosity method	• The two-phase mixed region can be described with the porosity. • The effective thermal conductivity of the mixture can be calculated as the volume average of the conductivities of porous matrix material and PCM • The porous media and fluid were not assumed to be in thermal equilibrium.	The effects of the structural parameters of the porous media and inlet conditions of HTF on the thermal performances of LHTES were numerically analyzed.	Experimental [98]
Shmueli et al. [99]	2D	Enthalpy porosity method	• Both solid and liquid phases were homogeneous and isotropic. • The melting process was axisymmetric.	The findings of the present study made it possible to define the heat transfer mechanisms from the tube wall to the liquid	Experimental [100]

Table 4 (*continued*)

Reference(s)	Dimensional	Numerical solution method	Assumptions	Comment	Validation
			• The molten PCM and the air were incompressible Newtonian fluids, and laminar flow was assumed in both.	PCM and then to the solid phase at various locations and instants.	
Ye et al. [101]	2D	Enthalpy porosity approach	• Density and dynamic viscosity of the PCM depended on temperature. • Variation of property values in liquid and solid phase PCM was imposed using piecewise linear interpolation. • Constant thermophysical properties were specified for aluminum.	The numerical study provided a detailed knowledge regarding interface heat transfer rate provides a deeper understanding the heat transfer mechanisms.	Experimental [102] and Numerical [103]
Tao and He [104]	2D	Enthalpy method	• The axial heat conduction and viscous dissipation in the HTF was negligible. • The flow of HTF was treated as one dimensional fluid flow. • The PCM region was treated as an axisymmetric model. • The effect of natural convection of PCM during melting was taken into account with an effective thermal conductivity of the liquid phase of PCM.	The effects of the non-steady inlet conditions of HTF on melting time, melting fraction, TES capacity, solid–liquid interface, heat flux on tube surface and HTF outlet temperature were analyzed.	Experimental [105]
Adine and Qarnia [106]	2D	Conservation energy equations Control volume approach	• The flow of HTF was dynamically developed. • The axial conduction and viscous dissipation in the fluid were negligible. • The thermophysical properties of the HTF and PCMs were independent of the temperature. • The thermophysical properties of solid and liquid phases of PCM were equal, except their thermal conductivities.	This parametric study could provide guidelines for system thermal performance and design optimization.	Experimental [105]

Apart from applying fins to PCMs, the effect of metal foams on heat transfer enhancement in rectangular encapsulated PCMs was investigated by Tian and Zhao [98] in 2011. The numerical investigation was based on the two-equation non-equilibrium heat transfer model, in which the coupled heat conduction and natural convection were considered at the phase transition and liquid zones. The numerical results were validated by experimental data. The main findings of the investigation were that the heat conduction rate increases significantly by using metal foams, due to their high thermal conductivities, and that natural convection is suppressed owing to the large flow resistance in metal foams. In spite of this suppression caused by the metal foams, the overall heat transfer performance is improved when metal foams are embedded into PCM. This implies that the enhancement of heat conduction offsets or exceeds the natural convection loss. The results also indicated that for different metal foam samples, heat transfer rate can be further increased by using metal foams with smaller porosities and bigger pore densities.

4.1.2. *Cylindrical containment models*

Three modes of cylindrical PCM container configurations are classified. The first model is the PCM filling the shell and the heat transfer fluid (HTF) flowing through a single tube (pipe model). In the second mode the PCM fills the tube and the HTF flows parallel to the tube (tube-tube model). The third cylinder model is the PCM encapsulated in a shell and HTF flows through the tube outside the shell to improve the heat transfer of PCMs (tube-shell model).

Ismail and Alves [119] numerically analyzed a pipe model with the PCM encapsulated in a shell while water as the HTF flowing through the tube. Radial conduction was assumed to be dominated during the process of solidification and the energy equation for the PCM was solved in conjunction with the equation governing the fluid bulk temperature as a function of time by employing the control-volume method. The effect of Biot number, ratio of diameters and inlet fluid temperature on the thermal performance of the storage unit were presented. Lacroix [105] developed an enthalpy based model to predict the transient thermal performance characteristics of a pipe LHTES with the PCM on the shell side and the HTF circulating inside the tube. Including the axial conduction effect in the PCM and employing an enthalpy based method, the coupled conservation equations governing the heat transfer in the PCM and HTF were solved iteratively using a finite-volume based finite-difference technique. Numerical results were presented for various thermal and geometric parameters such as shell radius, mass flow rate and inlet temperature of the HTF. It was concluded that for a given type of PCM, these parameters must be selected carefully in order to optimize the performance of the storage unit. Then the tube-tube model was theoretically studied by Esen and Durmus [120] in 1998. A theoretical model based on an enthalpy method was developed to predict the effects of various thermal and geometric parameters, configurations of the cylindrical container on the whole melting time for different PCMs. The theoretical results showed that the whole melting time of PCM depends on not only thermal and geometric parameters of the container, but also on the thermophysical properties of the PCM. It was found that a thicker PCM pack would result in longer melting time.

During 2006, Regin et al. [121] experimentally and numerically studied the third model that the melting behavior of paraffin wax encapsulated in a cylindrical capsule. The numerical analysis carried out by using enthalpy method and the results were verified with the experimental data. The experiments have been done by the visualization technique without disturbing the actual process

of melting. Numerical results indicated that the melting process is chiefly governed by the magnitude of the Stefan number, phase change temperature range and the capsule radius. The analysis showed that the agreement between the analytical and experimental results is significantly improved when the results are obtained by considering the phase change temperature range and the natural convection in the liquid phase instead of only considering the conduction heat transfer.

4.1.3. Spherical containment models

Generally, the PCM in the sphere is subjected to constrained (the solid and liquid phases have the same density) and unconstrained melting (the solid portion drops out of the melting layer due to its higher density).

The constrained melting of the PCM within a spherical container was investigated by Khodadadi and Zhang in 2001 [4]. The computations were based on an iterative, finite-volume numerical procedure by using the primitive-dependent variables, whereby the time-dependent continuity, momentum and energy equations in the spherical coordinate system were solved. With the buoyancy-driven convection gradually dominated the heat transfer mechanism due to the growth of the melt zone, the solid PCM melted faster in comparison to the bottom zone. When the buoyancy effects became remarkable, as many as three time-dependent re-circulating vortices were observed from the numerical simulation. The computational findings were verified through qualitative constrained melting experiments using a high-Prandtl number wax.

An experimental and computational investigation directed at understanding the role of buoyancy-driven convection during constrained melting of the PCM inside a spherical capsule was reported by Tan et al. in 2009 again [122]. The computations were based on an iterative, finite-volume numerical procedure that incorporated a single-domain enthalpy formulation for simulation of the phase change phenomenon. A Darcy's Law-type porous media treatment linked the effect of the phase change on convection. The computational predictions pointed to the strong thermal stratification in the upper half of the sphere that resulted from rising of the molten PCM along the inner surface of the sphere thus displaced the colder fluid. The measured temperature data and computational results near the bottom indicate the establishment of an unstable fluid layer that promotes chaotic fluctuations and is responsible for waviness of the bottom of the PCM. Regin et al. [123] also discussed an experimental and numerical study of a spherical capsule filled with a paraffin wax (melting temperature range of 52.9–61.6 °C) as the constrained PCM and placed in a convective environment during the melting process. Time-resolved temperature readings were obtained by using a rake of nine thermocouples that were placed on a horizontal plane passing through the center of the sphere. Keeping the initial temperature of the PCM constant, the temperature of the convective heat transfer fluid varied from 70 to 82 °C corresponding to Stefan numbers of 0.1143–0.2501. A 1D model for phase change by employing the enthalpy method and finite-difference formulation was developed. The model was then used to investigate the effect of capsule size and the Stefan number on the instantaneous heat flux, liquid fraction and melting time.

Considering the spherical geometries, apart from several analytical investigations of diffusion controlled phase change processes reported before 1980s, the first study on the unconstrained melting of the PCM within spherical container was carried out by Moore and Bayazitoglu [124] in 1982. A mathematical model was developed by assuming that the liquid remains at the fusion temperature during the whole period and solved by employing the perturbation method. The solid–liquid interface positions and the temperature profiles were determined for various Stefan and Fourier numbers. The experimental data agreed well with the simulation results. During 1987, Roy and Sengupta [125] performed a similar study and found an analytical solution for the melting rate at the lower surface of the solid PCM in contact with the heated surface. Later, Roy and Sengupta [126] performed another study on the unconstrained melting process inside a sphere. Two zones of the melting were identified: a thin melting layer at the bottom and a thicker layer at the top of the sphere. They found that a significant amount of melting took place at the upper surface due to the significance of natural convection, whereas in previous research [124,125], the effect of natural convection on the melting process was neglected.

4.2. Microencapsulated PCM

Micro-capsulation is a kind of tiny capsules (around 0.1–1000 μm in diameter) [127]. Micro-encapsulation has a higher heat transfer rates as compared to that of macro-encapsulation [128,129] due to a substantially higher surface area to volume ratio. Meanwhile, microencapsulation can tolerate the change in volume during phase change process [130]. Microencapsulation hence is a prominent technology for use of PCM in building materials. With the advent of PCM implemented in gypsum board, plaster, concrete and/or other wall covering materials, thermal storage can be part of the building structure even for light weight buildings.

4.2.1. Incorporation with building components

PCMs can be incorporated with gypsum board, plaster, concrete and/or other wall covering materials for the temperature control application purpose.

In general, storage density and phase change temperatures are very important parameters, since they determine the storage system size and human thermal comfort. Further, accurate estimation of the PCM enthalpy variation in the working temperature range is essential for correct mathematical modeling of the storage system [131].

The first research on the application of PCMs in buildings has been carried out by Telkes in 1975 [132]. $Na_2S0_4 \cdot 10\,H_20$ with a melting temperature of 32 °C was incorporated with walls, partitions, ceilings and floors to serve as temperature regulators.

Determination criteria for the optimal phase change temperature and storage density were provided by Zhou [133] as following:

$$T_{m,opt} = \overline{T}_r + Q/ht_{stor} \tag{26}$$

$$\overline{T}_r = t_d\, T_d + t_n T_n / t_d + t_n \tag{27}$$

$$D_{opt} = t_n h(T_{m,opt} - T_n)/\rho L \tag{28}$$

where $T_{m,opt}$ is optimal phase change temperature and D_{opt} is optimal thickness of the wall; Q represents the heat absorbed by unit area of the room surface; $\overline{T}_r$ is the average room temperature; t_{stor} is the heat storage time; the subscripts n and d represent night and daytime respectively.

Kuznik et al. [134] developed a one-dimensional model to optimize the thickness of phase change material only considering pure conduction. The simulation was based on a lightweight wall and interior/exterior temperature evolutions within a period of 24 h. The results showed that an optimal PCM thickness exists. With the optimal PCM thickness of 1 cm, the thermal inertia of the building was doubled and the PCM can reduce the temperature fluctuations inside rooms. To provide guidelines useful in selecting an optimal PCM for building wallboard, a numerical model was developed to determine the optimal melting temperature of PCM by Neeper [135]. The results indicated that the optimal melting temperature depends on the average room temperature. When the

melting temperature of PCM closed to the average room temperature, the maximum diurnal energy storage was achieved. Xiao et al. [136] established a simplified theoretical model to optimize an interior PCM for energy storage in a lightweight room. In this paper energy conservation equations were presented to calculate the optimal phase change temperature and the total amount of latent heat capacity. The analytical results agreed with Neeper's finding that the optimal melting temperature depends on the average indoor air temperature. Further, and it also depends on the radiation absorbed by the PCM panels.

A 1-D enthalpy model for analyzing the thermal performance of a shape-stabilized PCM floor was developed by Xu et al. [137]. By using the model, the influence of various parameters (melting temperature of PCM, thickness of PCM layer, latent heat of fusion, and thermal conductivity of PCM) on the thermal performance was analyzed by using a fully implicit the finite-difference method. It was found that for a given position or weather condition, the suitable melting temperature of PCM is roughly equal to the average indoor air temperature of sunny winter days, the heat of fusion and the thermal conductivity of PCM should be larger than 120 kJ/kg and 0.5 W/(m K), respectively, and the thickness of shape stabilized PCM plate used under the floor should not be larger than 20 mm. Zhou et al. [138] extended the investigation of the influence of various parameters from floor to walls and ceiling by using a verified enthalpy model. The model was validated by experimental work, and simulated results agreed well with the measured data. The numerical results showed that for the present conditions, the optimal melting temperature is about 20 °C and the heat of fusion should not be less than 90 kJ/kg, thin PCM plates with large areas are advantageous and the effect of PCM plates located at the inner surface of interior wall was superior to that of exterior wall (the south wall). A similar result to Xu et al. [137] was also obtained for the condition of the PCM wall and ceiling that the thermal conductivity should be larger than 0.5 W/(mK).

Athienitis et al. [139] experimentally and numerically studied the application of PCM in building envelope components for thermal storage. A 1-D non-linear enthalpy model was developed to simulate the transient heat transfer process in the walls using explicit finite difference scheme. The numerical result showed that the utilization of the PCM gypsum board may reduce the maximum room temperature by about 4 °C during the day time and can reduce the heating load at night significantly.

The numerical simulation of passive heating with PCMs was carried out by Chen et al. [140] by using a 1-D nonlinear mathematical model. The effective heat capacity method was used to simulate the PCM heat transfer problem by using the software MATLAB. The result indicated that applying proper PCM to the inner surface of the north wall in the ordinary room can not only enhance the indoor thermal comfort dramatically, but also increase the utilization rate of the solar radiation. Consequently the heating energy consuming is decreased and the goal of saving energy has been achieved. The energy-saving rate of heating season can get to 17% or higher.

4.2.2. Microencapsulated phase change slurry (MPCS)

Microencapsulated phase change slurry (MPCS) as a new technique has been getting more and more attention since this technique serves as both the heat transfer fluids and energy storage media. Consequently it can increase the thermal storage capacity and improve the energy efficiency of the thermal system. Due to the MPCS' increasingly important role, some review papers on the properties, heat transfer characteristics and application of MPCS have been published in recent years [127,141–143]. As a kind of suspension, the heat transfer and fluid flow characteristics of MPCS are different from those of the marco-encapsulated PCMs. In accordance to the review of Delgado et al. [142], the heat transfer characteristics of the MPCS can be classified into forced convection and natural convection.

4.2.2.1. Laminar forced convection heat transfer. The MPCS used to enhance convective heat transfer is generally laminar due to the high viscosity. Charunyakorn et al. [144] firstly conducted a numerical simulation of MPCS flow in circular tubes under different boundary conditions. The energy equation was formulated by taking into consideration both the heat absorption (and release) during phase transition and solved using an implicit finite difference method. Their parametric study showed that the bulk Stefan number and volumetric particle concentration are the two dominant parameters. Their model also showed that the heat transfer enhancement ratio of the fluid could be 2–4 times of that of water. Zhang and Faghri [145] modified the model of Charunyakorn [144] to include the effects of the microcapsule walls, initial sub-cooling and the melting temperature range. A temperature transforming model was used to solve the melting in the microcapsule by instead of a quasi-steady model. The numerical results showed a very good agreement with the experimental results of Goel et al. [146]. Their numerical results suggested that the differences between the experimental results of Goel et al. and numerical predictions of Charunyakom could be decreased greatly if these additional factors are considered. The authors however did not give any correlation or other similar criteria that could be used for future design.

Complicated source terms are applied to the theoretical models above to account for the phase change effects. In order to simplify the simulation process, Alisetti and Roy [147] developed a simpler effective specific heat model to study the heat transfer in MPCS. The results showed that the exact form of the specific heat function is not critical as long as the latent heat is incorporated correctly within a finite melting temperature range. Based on the concept of effective specific heat, Roy and Avanic [148] developed a model to analyze the laminar forced convection heat transfer to a PCM suspension in a circular duct under constant wall heat flux condition. The model has been verified with experimental data. The results demonstrated that Stefan number is the only parameter that has a significant impact on the thermal performance. Sub-cooling effect only can affect the heat transfer performance at very low heat fluxes or when the inlet temperature is much lower than the melting point. A simple correlation to predict the wall temperature rise as a function of the tube length was also developed for future design.

Hu and Zhang [149] introduced a model to provide a novel insight for the forced convective heat transfer enhancement of MPCS flowing through a circular tube with constant heat flux. The model was developed based on effective specific heat capacity method and used to analyze the influence of various factors on heat transfer enhancement. A modified Nusselt number was introduced since the conventional Nusselt number correlations for internal flow of single phase fluids are not suitable for accurately describing the heat transfer enhancement with MPCS. The modified local Nusselt number is inversely proportional to the dimensionless wall temperature. The numerical results indicated that the exact nature of the phase change process strongly affects the degree of convective heat transfer enhancement. The Stefan number and the PCM concentration resulted to be the most important parameters on the improvement of heat transfer in MPCS. Zeng et al. [150] analyzed experimentally and numerically the enhanced convective heat transfer mechanism of MPCS in the thermal fully developed range. An enthalpy model was proposed and developed for simulating the forced convective heat transfer characteristics of laminar flow with MPCS in a circular tube under constant wall heat flux. The results showed that in the phase change heat transfer region the Stefan number and the dimensionless phase change temperature range number are the

most important parameters influencing the Nusselt number fluctuation profile and the dimensionless wall temperature. The bulk fluid Reynolds number, particle diameter and the microcapsule volumetric concentration also influence the Nusselt number profile and the dimensionless wall temperature but are independent of the phase change process.

4.2.2.2. Turbulent forced convection heat transfer. A majority of past studies have considered laminar forced convection heat transfer to MPCM and only a few numerical investigations on turbulent forced convection heat transfer have been reported. However, the turbulent flows occur in majority of engineering applications of MPCS. In order to investigate the turbulent heat transfer to PCM suspensions, Roy and Avanic [151] presented an effective specific heat capacity model for PCM suspensions in a circular tube with constant heat flux under turbulent flow condition. The numerical results were found to agree with previously published experimental data and showed that this effective specific heat model can effectively model turbulent heat transfer with PCM suspensions. The most primary parameter in heat transfer was the Stefan number. The melt temperature range and degree of subcooling are other two important parameters. Royon and Guiffant [152] developed a numerical model to describe the thermal behavior of a slurry of PCM slurries flow in a circular duct under different flow parameters (Reynolds number). The simulation results demonstrated that the influence of Reynolds number on the minimum length of the heat exchanger is relatively weak.

4.2.2.3. Natural convection heat transfer. Inaba et al. [153] developed a 2-D model to study the fluid flow and heat-transfer characteristics for Rayleigh–Bénard natural convection of non-Newtonian PCM slurry. They found that Rayleigh number, Prandtl number and aspect ratio could be the primary factors for most of Newtonian and non-Newtonian fluids to evaluate the natural convection. A modified Stefan number was defined in the paper to evaluate the natural convection in a PCM slurry. Later, Inaba et al. [154] presented another 2-D model to study the natural convection heat transfer of a MPCS. It was found that the natural convection effect and heat transfer enhancement were due to the contribution of the latent heat transfer.

4.3. Summary of numerical models

It can be seen that the numerical models collected above for encapsulated PCMs all have their limitations. As the practical phase transformations in different applications are complicated, and the thermal conditions are not ideal. Various assumptions were set up for each numerical solution according to different numerical simulation purposes. There is none of numerical models can describe the phase change problem properly. Hence, the numerical modeling of LHTES only approximately approaches but not accurately presents the practical thermal performance of LHTES. Therefore, more investigation should be carried out to study the phase change problems so as to provide a more detailed insight of the actual heat transfer behaviors inside PCMs during the phase transformations.

5. Conclusions

This paper presented a comprehensive review of mathematical and numerical methods applied to the solutions of phase change problems. Firstly heat transfer mechanisms during the charging and discharging processes were discussed in this review. The heat transfer mechanisms play the most important role on the numerical results. Consequently, it is important to weight the percentages of conduction and convection heat transfer taken in each stage. Then, it presented the fundamental mathematical descriptions of the phase change phenomenon, the Stephan problem and Neumann problem. At last, a description of the numerical solutions for phase change problems based on considering only conduction and considering also convection. The PCMs have been applied in thermal energy storage applications widely due to their attractive features. Various numerical models for encapsulated PCMs in terms of macro-encapsulated and micro-encapsulated PCM were also analyzed in this paper. Nevertheless, the incorporation of PCMs in a particular application calls for an analysis that will enable the researcher to understand the heat transfer principle inside PCM correctly. From this survey, some further works are recommended:

- Further investigation should be carried out to obtain adequate knowledge of the phase change problems so as to minimize the assumptions made in the numerical models.
- Development of new numerical model to broaden its application in phase change problems and improve the accuracy of its results.
- Assessment of the stability and convergence on the numerical results is always required, and the numerical predictions should always be validated by using appropriate experimental data.
- Unified dimensionless parameters needs to be developed to make the gained knowledge applicable to other cases.
- Life cycle analysis, both economical and energetic feasibility of PCM application should be performed as LHTES is a more expensive form of thermal storage, but few scientific publications covered this matter.

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